DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the plating method of polyolefin-system-resin products. It is related with the method of plating to the substrate which uses comparatively small polyolefine of surface polarity as a principal member in detail.

[0002]

[Description of the Prior Art]Conventionally, the thing as shown below is known as this kind of art. That is, while a resin base material is fabricated first, plasma treatment and corona treatment are performed to the substrate. Refining of the surface of a substrate is carried out by processing of one of these, after that, it passes like the various usual platers and a plating layer is formed.

[0003]However, in this art, since the device and the approach were complicated and continuous processing was difficult, the whole work became inefficient. In the above-mentioned art, the substrate with which surface treatment processing of plasma treatment etc. was performed is offered like various platers after that. Naturally, although processing of degreasing, etching, etc. was also included, even if refining of the surface was carried out with much trouble in this case, a possibility that the effect of refining may be reduced by subsequent etching was like these various platers.

[0004]then, in the art indicated by JP,5-320928,A, for example, that by which one or more kinds of surface-active agents with small surface tension were added is describing the electroless plating liquid which consists of a copper ion, a reducing agent of a copper ion, and a complexing agent and a pH adjuster. By adopting this electroless plating liquid, it also enables ** to form an electroless plating layer in the base material surface of a fluoro-resin etc. not through surface treatment processing like the above.

[0005]

[Problem(s) to be Solved by the Invention]However, the above-mentioned art was very difficult to plate to the substrate which uses as a principal member polyolefines, such as polar small high density polyethylene etc. of that by which it is suitably adopted to the fluoro-resin for printed-circuit boards, etc., and in which it may deal. That is, as a method of plating to the substrate of a polyolefin system, it needed to pass through surface treatment processes, such as plasma treatment and corona treatment, as usual.

[0006]Are made in order that this invention may solve the above-mentioned problem, and the purpose, It is in providing the plating method of the possible polyolefin-system-resin products of forming a plating layer continuously and certainly as it is also with a comparatively simple device when plating to the substrate which used small polyolefine of surface polarity as the principal member.

[0007]

[Means for Solving the Problem]In [in order to attain the above-mentioned purpose] the invention according to claim 1, A process of fabricating a gross shape of a resin product by using polyolefine as a principal member, and obtaining a substrate, An etching process which etches the surface of said substrate, and a neutralization process which neutralizes the surface of said substrate which passed through an etching process, A surface treatment process of making said substrate which passed through a neutralization process contacting an ozone aqueous solution, and oxidizing said base material surface, A special neutralization process which processes said substrate which passed through a surface treatment process with a special neutralized solution which contains a cation system surface-active agent as the main ingredients, It is making into the gist to have had a catalyst grant process of giving a catalyst to the surface of said substrate which passed through a special neutralization process, and a nonelectrolytic plating process of forming an electroless plating layer in the surface of said substrate by contacting said substrate which passed through a catalyst grant process in a nonelectrolytic plating solution.

[0008]Here, a special neutralized solution in a special neutralization process is for containing a cation system surface-active agent represented by alkyl trimethylammonium chloride, for example as the main ingredients, and promoting adsorption to a base material surface of a catalyst in a next catalyst grant process.

[0009]Said catalyst grant process may be based on the catalyst -> Acre sweater method, and may be based on the sensitizing -> AKUCHIBESHON method.

[0010]In the invention according to claim 2, it is making into the gist to have established an electroplating process of forming an electroplating layer on an electroless plating layer formed in said substrate which passed through a nonelectrolytic plating process in a plating method of the polyolefin-system-resin products according to claim 1.

[0011]It combines and is making for said polyolefine to be polyethylene into the gist in the

invention according to claim 3 in a plating method of the polyolefin-system-resin products according to claim 1 or 2.

[0012]

[Function]According to the invention according to claim 1, the gross shape of a resin product is fabricated by using polyolefine as a principal member, and a substrate is obtained. In an etching process, the surface of said substrate is etched and a detailed crevice is formed on the surface of a substrate. In a neutralization process, the surface of the substrate which passed through the etching process is neutralized.

[0013]Next, in a surface treatment process, the substrate which passed through the neutralization process is contacted by the ozone aqueous solution, a base material surface oxidizes and refining is carried out. In a special neutralization process, the substrate which passed through the surface treatment process is processed with the special neutralized solution which contains a cation system surface-active agent as the main ingredients. In a catalyst grant process, a catalyst is given to the surface of the substrate which passed through the special neutralization process, and said crevice is adsorbed. here, pass a special neutralization process -- by being, it is easy to carry out the ionic bond of the crevice surface of a substrate to the catalyst which is tinged with minus charge, and adsorption of a catalyst is promoted more. And in a nonelectrolytic plating process, when the substrate which passed through the catalyst grant process is contacted by the nonelectrolytic plating solution, an electroless plating layer is formed on the surface of a substrate by using as a core said catalyst adsorbed and supported.

[0014]Now, in this invention, the substrate with which the surface treatment of the substrate passed through the neutralization process is contacted by the ozone aqueous solution. Therefore, it is carried out.

For this reason, a surface treatment process is continuously performed in like a series of platers as it is also with a comparatively simple device, and it deals in it.

[0015]While a base material surface oxidizes by surface treatment and a polar group is given to the surface, a surface crevice is adsorbed and many catalysts sell to it. Therefore, an electroless plating layer becomes that it is easier to be formed.

[0016]According to the invention according to claim 2, in addition to an operation of the invention according to claim 1, an electroplating layer is formed on the electroless plating layer formed in said substrate which passed through the nonelectrolytic plating process. For this reason, the whole plating layer serves as thickness and will become firm. Depending on the case, appearance will become good.

[0017]It combines, and according to the invention according to claim 3, though the polyethylene in which formation of a plating layer has been made comparatively difficult by the former in addition to the operation according to claim 1 or 2 was used as the principal member

of a substrate, a plating layer is formed easily and certainly and it gets.

[0018]

[Example]Hereafter, one example which materialized the 1 part slack fuel filler pipe of the car for this invention as a resin product is described based on a drawing.

[0019]Drawing 2 is a perspective view showing the fuel filler pipe 1 as a resin product in this example.

Drawing 3 is a typical sectional view fracturing and showing the part.

The fuel filler pipe 1 is for connecting between the fuel oil filler port of vehicles, and fuel tanks. The fuel filler pipe 1 is provided with the plating layer 3 which it comes to provide in the peripheral face of the pipe body 2 as a substrate, and the pipe body 2.

[0020]The pipe body 2 is fabricated, for example by the publicly known blow molding method by using high density polyethylene (HDPE) as a principal member. The pipe body 2 consists of the tubed body part 4 for leading the gasoline introduced mainly from the fill opening to a fuel tank, and the return section 5 for returning some gasoline to the upstream. Said plating layer 3 consists of an electroless plating layer and an electroplating layer. The electroless plating layer is formed in the thickness "0.3-1 micrometer" grade with nickel. An electroplating layer is formed in a thickness "20-30 micrometers" grade, and is formed of (neither being illustrated) with the strike plating layer which consists of nickel, a copper plating layer, a semigloss nickel plating layer, a lustrous nickel plating layer, and a chromium plating layer.

[0021]The metal retainers 6 are formed in the fill opening side of said body part 4. The flange 7 for attaching the fuel filler pipe 1 to a vehicle body is really formed in the center section of the body part 4.

[0022]Next, the surface treatment device which faces forming the plating layer 3 to the above-mentioned fuel filler pipe 1, and is used in some processes is explained. As shown in drawing 4, the surface treatment device 11 has a hose for connecting the ozone generator 12, the heater 13, the spray nozzle 14, the drain 15, and each member, etc. The ozone generator 12 can dissolve ozone underwater while changing oxygen to ozone. The ozone generator 12 can equip an inside with a pump (not shown), and can feed an ozone aqueous solution now to the direction of the heater 13. The heater 13 formed in the middle of the hose can warm now the ozone aqueous solution under flow even to a predetermined temperature.

[0023]The spray nozzle 14 which combined and was provided at the tip of a hose is allocated so that the warmed ozone aqueous solution which is sent from the heater 13 side may hit the pipe body 2 at spray state. It is desirable to have satisfied $A\text{-}B^{-2}>=0.07$, when distance of the tip of the spray nozzle 14 for setting spray pressure at the time of contacting an ozone aqueous solution to A (kPa) here, and injecting said ozone aqueous solution and the pipe body 2 is set to B (cm).

[0024]As for the drain 15, the conveyor for pipe body 2 conveyance is formed caudad.

The ozone aqueous solution after contacting the pipe body 2 is stored.
The ozone aqueous solution collected on this drain 15 is again introduced at a fixed speed via the interconnecting tube 16 to the ozone generator 12.
[0025]The relation of the solubility coefficient of ozone to the temperature of water is a relation as shown in drawing 5. That is, ozone becomes with the rise of the temperature of water that it is hard to dissolve, and ozone becomes with the rise of temperature that it is easy to be decomposed. It disagrees with this and the one where the temperature of water is higher is generally known that reaction velocity (surface treatment speed) increases. therefore, warming according to the heater 13 so that the concentration of ozone may become as high as possible as highly as possible in the temperature of an ozone aqueous solution -- it is desirable to make regulation suitably. As for the above-mentioned temperature, specifically, it is desirable that it is [not less than 65 **] 85 ** or less. As for the pH of the above-mentioned ozone aqueous solution, it is desirable that it is below "7." By being under an acid condition, it is because ozone in an ozone aqueous solution is hard to be decomposed and an ozone level can be raised more.
[0026]The pipe body 2 by which surface treatment was carried out with the surface treatment device 11 is offered to a subsequent catalyst grant process. Next, according to process drawing in which it is shown, it explains like the plater of drawing 1 about the manufacturing method for manufacturing the above-mentioned fuel filler pipe 1.
[0027]First, the above-mentioned pipe body 2 is fabricated with a publicly known blow molding method. Next, a PURAKON process is presented with said pipe body 2. That is, said pipe body 2 is made immersed for 125 seconds into 80 g/l of sulfuric acid, and the 60 ** solution containing 10 g/l of PURAKON. Then, the fat of the pipe body 2 surface is removed (degreasing), and bonded foreign matter is removed.
[0028]Then, an etching process is presented with the pipe body 2 which passed through the PURAKON process. That is, said pipe body 2 is made immersed for 604 seconds into the 65 ** solution containing 380 g/l of sulfuric acid, hexavalent chromium of 420 g/l, and trivalent chromium of 40 g/l. By passing through this processing, the pipe body 2 is etched and many detailed crevices are formed in the surface.
[0029]A neutralization process is presented with the pipe body 2 which passed through the above-mentioned etching process. That is, said pipe body 2 is made immersed for 60 seconds at a room temperature into the solution containing chloride 60 m/l, CR-200(chromium waste-liquid-treatment agent)8ml, and 2 g/l of hydrazine sulfate. Then, acid adhering to the surface of the pipe body 2 is neutralized.
[0030]Next, the surface of the pipe body 2 is reformed using the surface treatment device 11 grade mentioned above. That is, the pipe body 2 is moved to the right direction of drawing 4 by conveyor, and it offers to the surface treatment device 11. The ozone aqueous solution of

spray state is contacted by the pipe body 2 at this time. The surface of the pipe body 2 oxidizes and is polarized by the oxidizing power of the ozone which remains in underwater [accompanying this contact]. Though the pipe body 2 is making what kind of shape (this example shape of a pipe) at this time, an ozone aqueous solution becomes possible [the thing of the pipe body 2 certainly contacted to all the surfaces of a design surface at least]. Therefore, in each surface of the pipe body 2, oxidation reaction is performed uniformly and the reaction spots in each part cannot get up easily. Said pipe body 2 is rotated and it may be made to apply the ozone aqueous solution of spray state uniformly using the slewing mechanism etc. which are not illustrated in order to improve the homogeneity of the above-mentioned oxidation.

[0031]and the pipe body 2 by which surface treatment was carried out as mentioned above -- the next -- it offers to a special neutralization process. The pipe body 2 which passed through the surface treatment process Namely, cation system surface-active agent (let alkyl trimethylammonium chloride be the main ingredients in this example) 30 ml/l, Said pipe body 2 is made immersed for 242 seconds into the 50 ** solution containing B-200 (surface control agent) 30 ml/l. while the pipe body 2 is again neutralized by passing through this processing -- the next -- adsorption of the catalyst in a catalyst grant process comes to be promoted.

[0032]Then, a catalyst grant process is presented with the pipe body 2 which passed through the above-mentioned special neutralization process. The catalyst grant process in this example consists of a catalyst process and an accelator process. That is, the pipe body 2 which passed through the special neutralization process is made immersed for 215 seconds in a catalyst process into the 34 ** solution containing sulfuric acid 180 ml/l and catalyst C (catalyst grant agent)30ml/l. Then, the surface of the pipe body 2 and especially the part in which the crevice was formed by etching are adsorbed in palladium and a tin (Pd-Sn) complex compound.

[0033]The pipe body 2 is made immersed for 208 seconds in an accelator process into sulfuric acid 100 ml/l, 2 g/l of hydrazine sulfate, and the 45 ** solution containing accelator X(activation accelerator)0.5 g/l. Then, tin of the Pd-Sn complex compounds is removed, palladium is metalized, and a catalyst core is formed.

[0034]Next, a nonelectrolytic plating (electroless nickel plating) process is presented with the pipe body 2 which passed through the above-mentioned catalyst grant process. That is, the pipe body 2 is made immersed for 553 seconds into the 33 ** solution containing 6 g/l of metallic nickel, 18 g/l of sodium hypophosphite, 60 g/l of sodium phosphite, and 30 g/l of nickel sulfate. Then, the electroless plating layer which consists of nickel is formed.

[0035]Then, an electroplating process is presented with the pipe body 2 which passed through the nonelectrolytic plating process. Here, the various plating solutions at the time of forming each metal plating which constitutes the above-mentioned electroplating layer are explained.

First, the plating solution at the time of forming the strike plating layer which makes the bottom of the heap of an electroplating layer contains 250 g/l of nickel sulfate, 30 g/l of nickel chloride, and 30 g/l of boric acid. The plating solution at the time of forming a copper plating layer contains 200 g/l of copper sulfate, 50 g/l of sulfuric acid, 0.01 g/l of chloride, and a small amount of brightening agents. The plating solution at the time of forming a semigloss nickel plating layer contains 280 g/l of nickel sulfate, 45 g/l of nickel chloride, 40 g/l of boric acid, and a small amount of brightening agents. Combining, the plating solution at the time of forming a lustrous nickel plating layer contains 240 g/l of nickel sulfate, 45 g/l of nickel chloride, 30 g/l of boric acid, a small amount of brightening agents, and an additive agent. In addition, the plating solution at the time of forming a chromium plating layer contains 250 g/l of chromic anhydrides, 10 g/l of sodium silicofluoride, and 1 g/l of sulfuric acid.

[0036]And while making these each solution immerse the pipe body 2 in which the electroless plating layer was formed one by one, a predetermined time electrical-and-electric-equipment target is made to flow in each stage. Then, the electroplating layer which becomes order from the bottom from a strike plating layer, a copper plating layer, a semigloss nickel plating layer, a lustrous nickel plating layer, and a chromium plating layer is formed, and the plating layer 3 which consists of an electroless plating layer and an electroplating layer is formed. Then, after passing through a washing process etc., the fuel filler pipe 1 in which it comes to form the plating layer 3 in the pipe body 2 surface is obtained as a result.

[0037]As explained above, in this example, surface treatment of the pipe body 2 is performed, when the pipe body which passed through the neutralization process is contacted by the ozone aqueous solution. For this reason, a surface treatment process is continuously performed in like a series of platers as it is also with the comparatively simple surface treatment device 2, and it deals in it. As a result, while being able to attain remarkable simplification of cost, remarkable improvement in workability can be aimed at.

[0038]By passing through this surface treatment process, the pipe body 2 surface oxidizes and a polar group is given to the surface. By passing through a special neutralization process, a surface crevice is adsorbed and many catalysts sell to it. Therefore, the electroless plating layer in a nonelectrolytic plating process becomes that it is easier to be formed, and can form the plating layer 3 certainly. As a result, also in the pipe body 2 made from polyethylene (HDPE is included) made difficult [formation of plating] former comparatively, the plating layer 3 can be formed easily and certainly like this example.

[0039]In this example, the electroplating layer was formed on the electroless plating layer. For this reason, the plating layer 3 whole becomes a thick film and a dense thing further, and will become firm. Therefore, in the product in which high gas barrier property is demanded, the penetration of fuel, such as gasoline, can be certainly prevented like the fuel filler pipe 1 of this example.

[0040]In order to check the above-mentioned effect, the examination which measures fuel transmission quantity was done. Under the present circumstances, the thing as shown in drawing 6 was used as one of the devices which measure transmission quantity. That is, the transmission quantity measuring device 21 is provided with the cup 22 and the porous plate 23 which have the flange 22a. And it is concluded by the bolt 25 and the nut 26 where the specimen 24 (for example, monotonous piece of the fuel filler pipe 1 of this example) is pinched with the cup 22 and the porous plate 23. In the inside of the cup 22, it is fuel (put into 9:1 mixed liquor of MTBE10% mixed gasoline and ethanol.). And the transmission quantity of the fuel per [in predetermined time (for example, one day)] unit area was measured every specimen 24.

[0041]The result is shown in drawing 7. PE shows polyethylene among a figure, FKM shows fluorocarbon rubber, and a sealer shows what carried out orientation of the nylon to the shape of a folia into HDPE. According to the specimen (substrate + plating layer of HDPE) of this example, transmission quantity was "0" as shown in the figure. Also from this, according to the plating method of this example, while being able to form the plating layer 3 certainly, it can be said by the plating layer 3 that the penetration of fuel can be controlled certainly.

[0042]It combines, and in the surface treatment process of this example, since an ozone aqueous solution hits spray state on the surface of the pipe body 2, the quantity of the ozone per unit time which hits the pipe body 2 surface will become comparatively large. For this reason, the time to which an ozone aqueous solution is contacted as a whole can be extremely managed in a short time compared with the case where the resin-molding thing is made immersed into an ozone aqueous solution. Therefore, it becomes what good plating junction nature is obtained for as short-time reforming treatment is also (the plating layer 3 joins firmly). As a result, remarkable improvement in productivity can be aimed at.

[0043]This invention is not limited to the above-mentioned example, for example, may be constituted as following.

(1) In said example, although the fuel filler pipe 1 was adopted as a resin product, shape may be taken to other resin products (for example, inner, exterior equipments, etc. for cars, such as a front grille, a door mirror bracket, and a mark plate).

[0044]Even though it applies to the same fuel filler pipe 1, the shape is not limited to the thing of the above-mentioned example at all. Therefore, it does not interfere at all as composition which omits the return section 5, the retainer 6, and flange 7 grade, for example.

[0045](2) In said example, although HDPE was adopted as a principal member as polyolefine, don't deviate from other polyolefines, for example, usual polyethylene, low density polyethylene, polypropylene, etc. from the meaning of this invention as a principal member.

[0046](3) Although the pipe body 2 was fabricated with the blow molding method, the usual injection molding etc. may be fabricated in said example by what kind of method.

(4) Although the electroless plating layer and the electroplating layer constituted the plating layer 3 from said example, it is good also as composition which omits an electroplating layer. That is, if at least an electroless plating layer can fully exhibit the function but, it is good also as a plating layer only with an electroless plating layer.

[0047]The presentation of each plating layer and the solution for plating and the thickness of plating are not limited to the thing of the above-mentioned example at all. Therefore, a presentation can be changed according to the occasional purpose use.

[0048](5) As long as it contacts an ozone aqueous solution to a base material surface in short, it may be made to contact by what kind of method, although the ozone aqueous solution was put in said example to the surface of the pipe body 2 in the surface treatment process at spray state. For example, it may be made to guess in the shape of a waterfall, and may be made to make a substrate immersed into the container with which it comes to store an ozone aqueous solution.

[0049](6) After fabricating the pipe body 2 in said example, it was made to present a PURAKON process in it, but even if it skips the process concerned, don't interfere.

(7) Although alkyl trimethylammonium chloride was mentioned as an example of representation as a surface-active agent of a cation system, also out of it, polyoxyethylene alkylamine, alkyldimethyl benzylammonium chloride, etc. are adopted suitably, and sell them at said example.

[0050](8) the treatment temperature in each down stream processing in said example, processing time, processing important point medicine, etc. are not limited to the thing of the above-mentioned example, and are the thing which is sometimes boiled, and it responds and can be changed.

[0051](9) Although the method of consisting of a catalyst process and an accelator process was used for the catalyst grant process, it may be made to give a catalyst by the sensitizing process and an AKUCHIBESHON process in said example.

[0052](10) In said example, in some processes, although the example which conveys the pipe body 2 by conveyor was introduced, conveyance by the hanger usually adopted like a series of platers may be adopted.

[0053]It is not indicated to each claim of a claim and the technical idea which can be grasped from the above-mentioned example is indicated with the effect below.

(a) Said substrate which passed through the neutralization process was made to contact the ozone aqueous solution of spray state in said surface treatment process in the plating method of the polyolefin-system-resin products according to any one of claims 1 to 3. By having the above-mentioned composition, the very good surface treatment effect is acquired for a short time, and the effect that positive formation of a plating layer can be promoted is done so.

[0054]

[Effect of the Invention]As explained in full detail above, according to the plating method of the polyolefin-system-resin products of this invention, the outstanding effect that a plating layer can be formed continuously and certainly as it is also with a comparatively simple device is done so when plating to the substrate which used small polyolefine of surface polarity as the principal member.

[Translation done.]